

# **Report for 2002IA16G: Relationship of Nitroso Compound Formation Potential to Drinking Source Water Quality and Organic Nitrogen Precursor Source Characteristics**

- Dissertations:
  - Assuoline, Jason, 2004, An Exploratory Study of the Formation of N-Nitrosodimethylamine (NDMA) in Chloraminated Natural Waters, MS Thesis, Dept. of Civil & Environmental Engineering, University of Iowa, Iowa City, Iowa.

Report Follows

# **Relationship of Nitroso Compound Formation Potential (NCFP) to Drinking Source Water Quality and Organic Nitrogen Precursor Source Characteristics**

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## **Problem and Research Objectives**

Recent research indicates that certain disinfection practices may result in the formation of significant amounts of N-nitrosodimethylamine (NDMA) and, quite likely, other nitroso compounds in drinking water. These compounds are believed formed when chlorine is added to water containing ammonia and certain organic nitrogen compounds ("precursors"). Measurements in several drinking water distribution systems suggest that unprotected sources receiving point and non-point waste discharges are particularly susceptible to their formation, especially when chloramination is practiced.

The formation of NDMA and possibly other nitroso compounds in drinking water is an emerging concern because they are generally carcinogenic, mutagenic, and teratogenic (Loeppky et al., 1994; O'Neill et al., 1984). For example, the nitrosamine, N-nitrosodimethylamine, NDMA ( $\text{CH}_3)_2\text{NNO}$ ) is a particularly potent carcinogen. Risk assessments from California's Office of Environmental Health Hazard Assessment (OEHHA) and US EPA identify lifetime de minimis (i.e.,  $10^{-6}$ ) risk levels of cancer from NDMA exposures as 0.002 ppb (2 ng/L) and 0.0007 ppb, respectively. In February of 2002 the California Department of Health Services established an interim action level of 0.01 ppb (10 ng/L) in drinking water.

Many drinking water sources in the Midwest and other parts of the country are unprotected receiving point and non-point waste discharges. Municipal and industrial waste discharges, and those associated with agricultural practices, are potentially important sources of the organic nitrogen precursors required for the formation of nitroso compounds. These waters are correspondingly expected to be susceptible to nitroso compound formation from chloramination. This may limit the use of some water sources for drinking water or restrict treatment options that otherwise have desirable characteristics. Initial observations indicate that some consumers are being exposed to undesirable levels of NDMA. Organic nitrogen is therefore not a simple, benign pollutant typically associated with nutrients as generally thought.

A need exists for an improved understanding of the nature and extent of this potential problem. Work is especially needed that relates nitroso compound formation potential to source water quality and origin of organic nitrogen precursors, watershed uses, and to biogeochemical processes that could influence the quantity and types of nitroso compounds potentially produced.

Based upon the ascertained research needs, the following specific objectives of this research study have been formulated with respect to the relationship of source water quality and nitroso compound formation potential (NCFP) as a newly recognized disinfectant by-product:

1. Characterize the NCFP in a variety of "susceptible" surface and groundwater drinking source waters.
2. Examine the relationship of NCFP to source water quality and land usage.
3. Conduct mechanistic studies to characterize precursors and the influence of potentially important physical, chemical, and biological processes of the NCFP.

## **Methodology**

**Overview.** The primary focus of the work performed to date has been the measurement of NDMA "Formation Potential" (NDMAFP) in natural water samples obtained from a variety of agriculturally impacted sources in Iowa. The sample locations along various rivers were selected because they were identified as points within watersheds categorized by the USGS as bodies of water impacted by agricultural waste discharges. The NDMAFP was determined through a series of laboratory assays which focused on the amendment of the surface water samples with the disinfectant monochloramine ( $\text{NH}_2\text{Cl}$ ). The NDMAFP in river water samples was examined by season and in relation to other water quality variables such as nitrite, nitrate, and organic nitrogen concentrations. Additional studies were conducted to delineate the potential importance of DMA as an identifiable NDMA precursor versus other unidentified nitrogenous substances.

An additional activity was an investigation of the influence of riverbank filtration (RBF) on the formation of NDMA after chloramination. RBF is a practice in which drinking water is withdrawn from shallow wells near a river. As such, the water is subjected to a variety of biogeochemical processes that influence its water quality. While RBF is effective at reducing the formation of many halogenated DBPs such as THMs and HAAs, the relationship between riverbank filtration and NDMA precursor removal is not known.

**Source Waters.** Surface waters were sampled monthly from April 2003 to February 2004 at four locations categorized by the USGS as being substantially impacted by agricultural runoff and waste discharges (Table 1). The relative agricultural impact at each sampling site was estimated based on historical data representing average nitrite+nitrate ( $\text{NO}_2+\text{NO}_3$ ) data found on the USGS website (NAWQA website) for years 1996 to 2002.

Table 1 Summary table of USGS-NAWQA sampling locations used throughout the course of this study. Four liters of water were collected from each site near the beginning of each month in 1 liter amber bottles which were stored at 4°C until analyzed. The relative agricultural impact ranking has been assessed by average NO<sub>2</sub>+NO<sub>3</sub> for each site.

Station Number	Station Name	Historical* NO <sub>2</sub> +NO <sub>3</sub> in mg/L as N	Relative Agricultural Impact**
05420680	S. Fork Iowa River NE of New Providence	9.19	1
05465500	Iowa River near Rowan	7.05	2
05449500	Wapsipinicon River near Tripoli	5.61	3
05451210	Iowa River at Wapello	4.72	4

\* Historical data represents the average NO<sub>2</sub>+NO<sub>3</sub> values based on monthly measurements taken from 1996 to 2002.

\*\* 1=highest, 4= lowest

In this study, the influence of riverbank filtration on NDMA formation potential of two typical Midwestern river supplies was examined. Both facilities use similar treatment processes within the plant; however, minor differences in treatment process do exist. The IC treatment facility is located nearly 30 miles south of the CR plant in Southeastern Iowa. The IC plant is located on the Iowa River, where 2 well fields containing a total of 4 horizontal wells draw water through a previously pristine alluvial aquifer. The CR facility has three large well fields stretching along a meandering segment of the Cedar River where a combination of more than thirty vertical wells supplies water to the treatment facility. While this plant and its various wells have been operating for nearly 20 years, blending waters with a range of turbidity, organic carbon and other water quality characteristics, the IC facility came on line in 2003, during the course of this study.

Another difference between the two plants is that they use different chemical disinfectants. While both facilities originally planned to use chloramines, the IC plant, since it began using riverbank filtration, is able to rely solely on free chlorine to provide the required disinfectant dose while remaining within the guidelines of the Disinfectant/Disinfection By-Product Rule designated by the recent SDWA amendments. However, it should be noted that ammonia levels entering the plant are often substantial enough to lead to the incidental formation of monochloramine upon the addition of chlorine. This may have implications on NDMA occurrence at these facilities even in the absence of intentional chloramine usage.

Water samples were obtained from the raw river water and from monitoring wells located at several locations representing a span of hydraulic residence times. Water samples were also collected from several in the treatment plants. Table 2 summarizes the characteristics of two vertical wells which feed the 60 MGD CR treatment facility. Not all wells are operated continuously, yet in this study the same wells were sampled each time. The

wells were selected because the water residence times differed greatly as estimated by the (USGS, 1995). The IC plant began full scale operation in October 2003 and therefore, sampling in November was one of the first times the wells were sampled after they had been in full service. The IC wells were situated about 50 feet from the banks of the Iowa River, and the horizontal sections of the collection wells extended from the wells, under the river. However, it was not feasible to estimate specific residence time within the aquifer since detailed hydraulic characterization for the new IC wells was not readily available for this study.

Table 2 Hydrogeologic characteristics for Seminole well field. Estimated travel time was calculated based on the distance from the well to the river and the approximate hydraulic conductivity initially measured at each specific well.

Sampling Well	Distance From River (ft)	Hydraulic Conductivity (ft/d)	Transmissivity (ft <sup>2</sup> /d)	Specific Capacity (gpm/ft)	Estimated Travel Time (d)
Seminole 14	800	57.2	3,374	25.4	<b>14</b>
Seminole 17	63	192.7	11,177	73.1	<b>0.33</b>

**Analytical Methods.** The basis of the NDMA FP test has been described by Mitch and Sedlak, 2004. It is based upon addition of preformed monochloramine to water samples and a 7-day reaction time. The use of preformed monochloramine instead of the usual practice of in-situ formation by addition of free chlorine and followed by ammonia addition maximizes NDMA formation. Additional work (results not shown) indicated that NDMA formation was reduced significantly by pre-chlorination. While this suggests a strategy to reduce NDMA formation, it nonetheless creates an artifact difficult to control.

The first step in preparing the reactors was filtering the water samples through Millipore AP25 glass fiber filter designed to remove particles greater than 0.8-1.6  $\mu\text{m}$  in size. Next, the filtered water was measured into the reactor jars so that the final volume of the solution containing sample water, buffer, and  $\text{NH}_2\text{Cl}$  would be 500 mL. Concentrated buffer solutions were used to create pH stability in the reactors throughout the incubation period. A 10 mM phosphate buffer was used for the lower pH 7 while 10 mM bicarbonate was added to maintain a pH near 8. These two pH levels were used in the agriculturally impacted surface water samples, however only the bicarbonate buffer was used for the riverbank filtration reactors. Blank samples for every site were amended with the appropriate buffer to form the same concentration as the reactors spiked with 1mM  $\text{NH}_2\text{Cl}$ . Duplicates were run when there was sufficient sample volume collected. Concentrated monochloramine stock solution with a 0.1 Cl/N molar ratio was prepared fresh prior to each experiment by addition of reagent grade ammonia and hypochlorous

acid to a pH 10 solution containing 10 mM bicarbonate. Dosages added to the reactors ranged from 0.05 mM to 1 mM. The  $\text{NH}_2\text{Cl}$  was measured in control samples on a daily basis in order to ensure that high levels were present throughout the incubation period.  $\text{NH}_2\text{Cl}$  concentrations were determined by DPD-FAS titrimetric method (APHA, AWWA, and WEF; 1998).

Experiments were initiated by addition of the preformed monochloramine at a high dose of 1 mM, or 71 mg/L as  $\text{Cl}_2$  was added to all agricultural watershed samples (approximately 20 times that of the typical residual allowed in drinking water distribution systems as dictated by the Stage 1 Disinfection/Disinfectant By-Product Rule). A much lower dosage of 0.05 mM was added to some of the riverbank filtration samples to mimic typical dosages used to maintain a substantial residual throughout a distribution system (approximately 4 mg/L as  $\text{Cl}_2$ ).

All samples were incubated in the dark for 7 days (168 hours) at 20°C. Reducing light exposure to the samples as much as possible ensured that the quantity of NDMA formed would not be significantly affected by photodegradation. After the 7-day incubation period, the final pH was measured to ensure buffer stability and minimal pH variation throughout the assays. A solid/liquid extraction process was used to concentrate the NDMA formed into a small volume of methylene chloride for analysis (Luo and Clevenger, 2003 and Taguchi et al., 1994). An internal standard of d6-NDMA was added to each reactor to form a baseline concentration of 100 ng/L. This internal standard, in conjunction with calibration curves developed for each assay, facilitated the subsequent quantification of these experiments.

NDMA was measured with a Varian GC CP3800 coupled with a Saturn 2200 MS/MS detector. The column used is Varian gas chromatograph had a length of 30 m, film thickness of 0.25  $\mu\text{m}$  and insider diameter of 0.25 mm. The general temperature ramping protocol for the GC started with a temperature of 35°C for 4 minutes. Next, the temperature was increased to 140°C at a rate of 20°C/min. A secondary ramp elevated the temperature to 200°C at a rate of 50°C/min. This temperature was held for 9.55 minutes. The total time each sample was 20 minutes. The Saturn 2200 MS/MS detector was used under the following settings: m/z 81 for quantification of d6-NDMA and m/z 75 for NDMA.

Glassware used in the experiments was washed thoroughly with warm tap water, soaked in a nitric acid bath and then rinsed again with copious quantities of deionized (DI) water. After washing, the glassware was baked in a muffle furnace at 500°C for 1 hour. All solutions were prepared using DI water obtained from a Barnstead ROPure Infinity™/NANOPure Diamond™ system (Barnstead/Thermolyne Corp., Dubuque, IA). This treatment system produced water with a target resistivity of 18.2  $\text{m}\Omega\text{-cm}$  and [TOC]  $\leq 3$  ppb. All chemicals purchased and used in this study were ACS reagent grade and properly stored.

## **Principal Findings and Significance**

**NDMA Formation Potential in Watershed Samples.** Figure 1 and Figure 2 are box and whisker plots showing the mean, quartile and extreme NDMA FP from July to February at each of the four locations sampled during this study. The extreme values at each site were fairly broad and ranged from 12.5 to 145.4 ng/L. Mean values for each site and at each pH value ranged from 45.6 to 92.9 ng/L. Despite significant fluctuations in the levels of NDMA formed in these samples, concentrations measured were consistently above the 10 ng/L California action level. This broad spectrum of measured NDMA in the reactors illustrates the role that fluctuations in water quality may play in the ultimate NDMA formation of a given water source. While avenues of this study are ongoing and some conclusions can be made from these results, seasonal trends were not apparent over this year. As aspects of this study continue based on these preliminary findings, seasonal trends may become more obvious.

Among the reactors tested in each sampling period, it should be noted that nearly all blank samples, those containing only sample water and buffer with no  $\text{NH}_2\text{Cl}$ , did not produce measurable levels of NDMA. This strongly suggests that background levels of NDMA in the source water for each sampling point was negligible throughout the course of the experiment and therefore NDMA formation was induced by the addition of  $\text{NH}_2\text{Cl}$ .

The relative agricultural impact of these watersheds was initially assessed based on total organic carbon (TOC), nitrite + nitrate ( $\text{NO}_2 + \text{NO}_3$ ) and organic nitrogen measurements performed by USGS scientists on historical samples. Relative agricultural impact for each sample location was based on the levels of these telltale water quality parameters as well as known agricultural operations in the area (see Table 1). The majority of historical data spans sample dates from 1996 until August, 2002. These parameters were not measured during this study; however, agricultural practices in the areas have not significantly changed since 2002. Statistical plots for the samples presented in Figures 1 and 2 suggest that there is no particular correlation between the relative agricultural impact on the watershed and NDMA formation because NDMA was consistently formed for all samples. A specific minimum threshold for these parameters influencing NDMA formation was not determined. Nonetheless, the fact that high levels of consistently quantifiable NDMA were formed suggests that these agricultural impact parameters play a role in the formation of NDMA when the samples are amended with  $\text{NH}_2\text{Cl}$ .

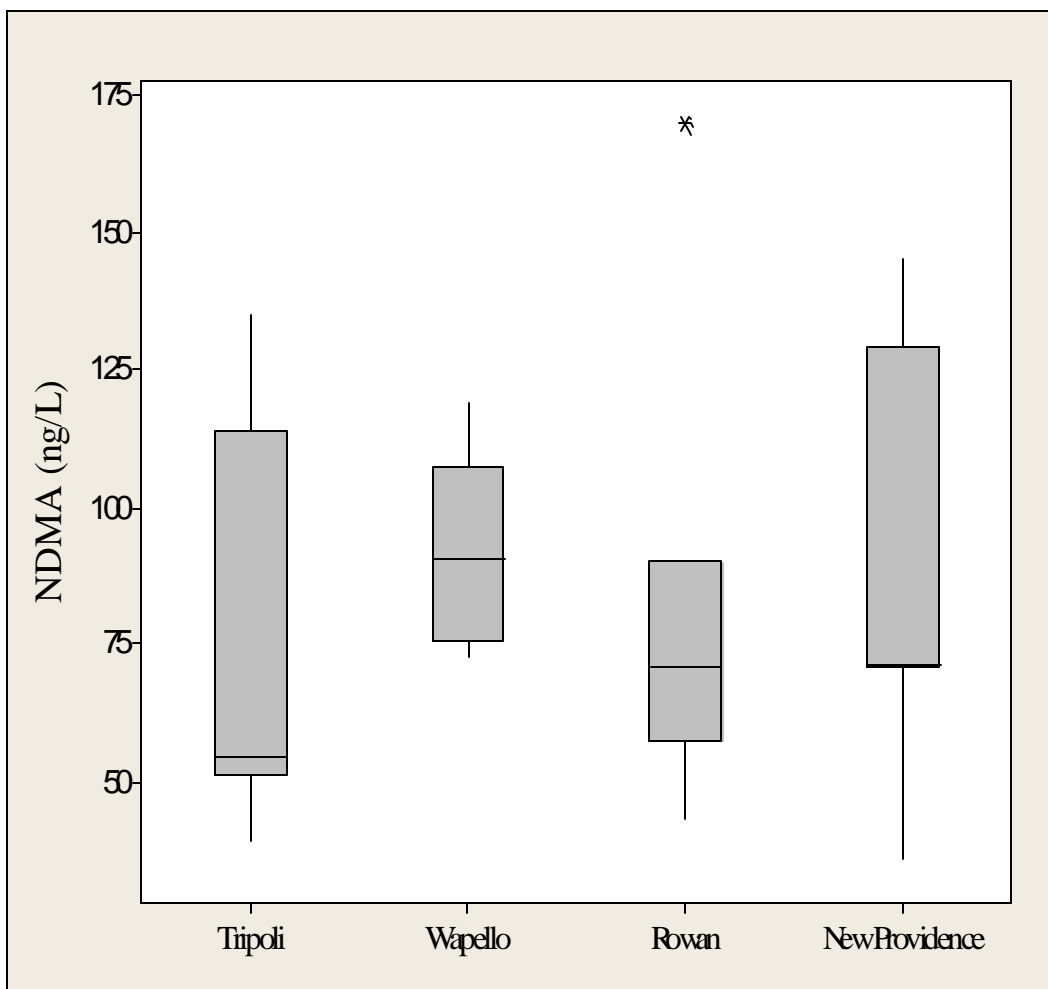


Figure 1. Box plot representing NDMA formation potential at pH~8 for each site pooled over the course of this study. The extremities of the whiskers show minimum and maximum NDMA formation potential at each site while the boxes define the quartile values and the median value. The “\*” represents the outlier NDMA value measured in one of the Rowan sample months.



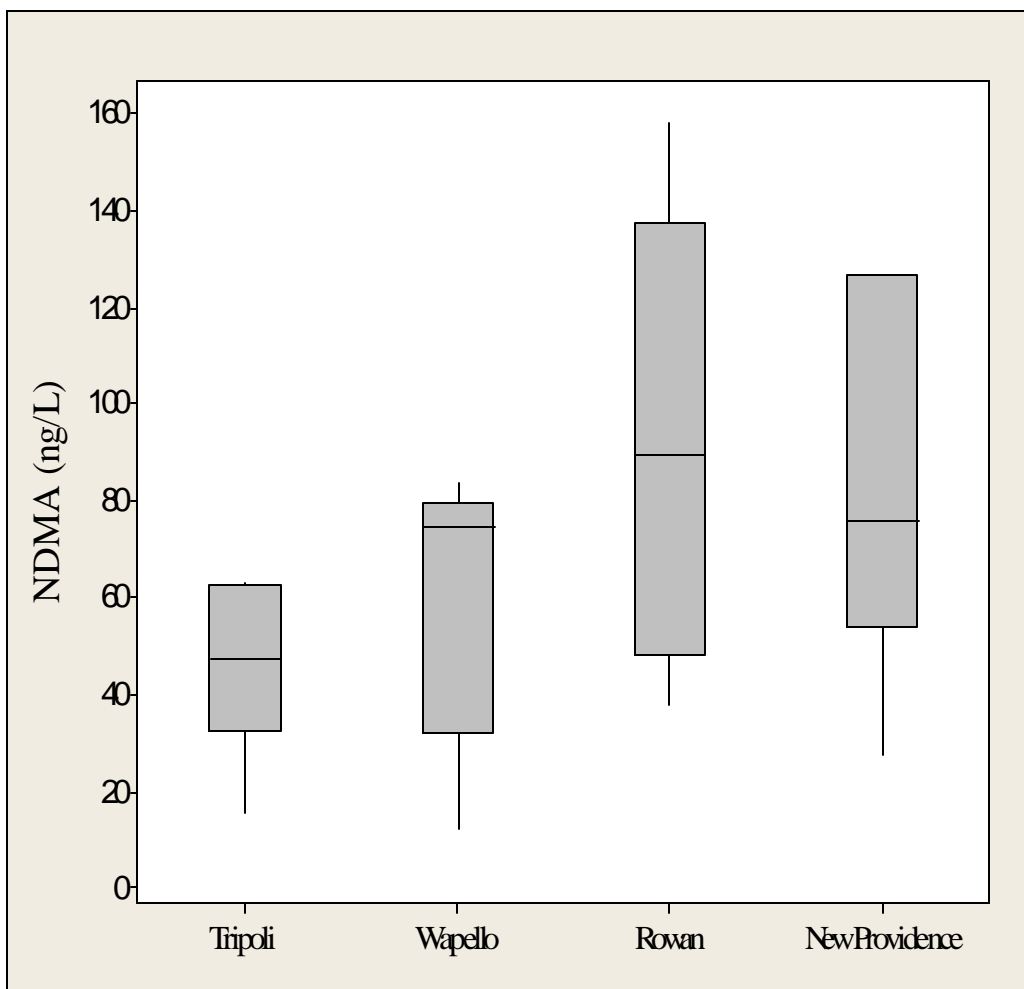


Figure 2. Box plot representing NDMA formation potential at pH~7 for each site pooled over the course of this study. The extremities of the whiskers show minimum and maximum NDMA formation potential at each site while the boxes define the quartile values and the median value.

**Riverbank Filtration.** The riverbank filtration samples shown in this section exhibit results from watersheds which are not directly influenced by agricultural practices, but can nonetheless have high levels of TOC,  $\text{NO}_2 + \text{NO}_3$  and  $\text{NH}_3$  due to the migration of these parameters throughout surface waters in the state of Iowa. This can be seen in the levels of NDMA formed in the raw water (original surface water source for each facility) samples, which remained within the range previously observed in the samples defined as directly impacted by agricultural practices. Results from the samples collected from various locations at each of the two treatment facilities are shown in Figures 3 and 4.

Representative plots are presented (Figures 3 and 4) to show NDMA formation trends observed in several sampling events. In these graphs it can be seen that NDMA formation was significantly reduced by riverbank filtration at both the IC and CR locations when the high dose of 1 mM monochloramine was added. The NDMA levels dropped from 102 ng/L to 15 ng/L and 64 ng/L to 24 ng/L between the raw river water and the well

samples. Interestingly, further conventional treatment did not appear to influence the NDMA FP at the higher  $\text{NH}_2\text{Cl}$  dose.

In contrast, neither riverbank filtration nor conventional treatment had a significant impact on NDMA formation when it was measured using the more practically significant monochloramine dose of 0.05 mM. Under these lower monochloramine dosage levels,  $\text{NH}_2\text{Cl}$  exhaustion may be occurring before the precursor reservoir in each sample is consumed.

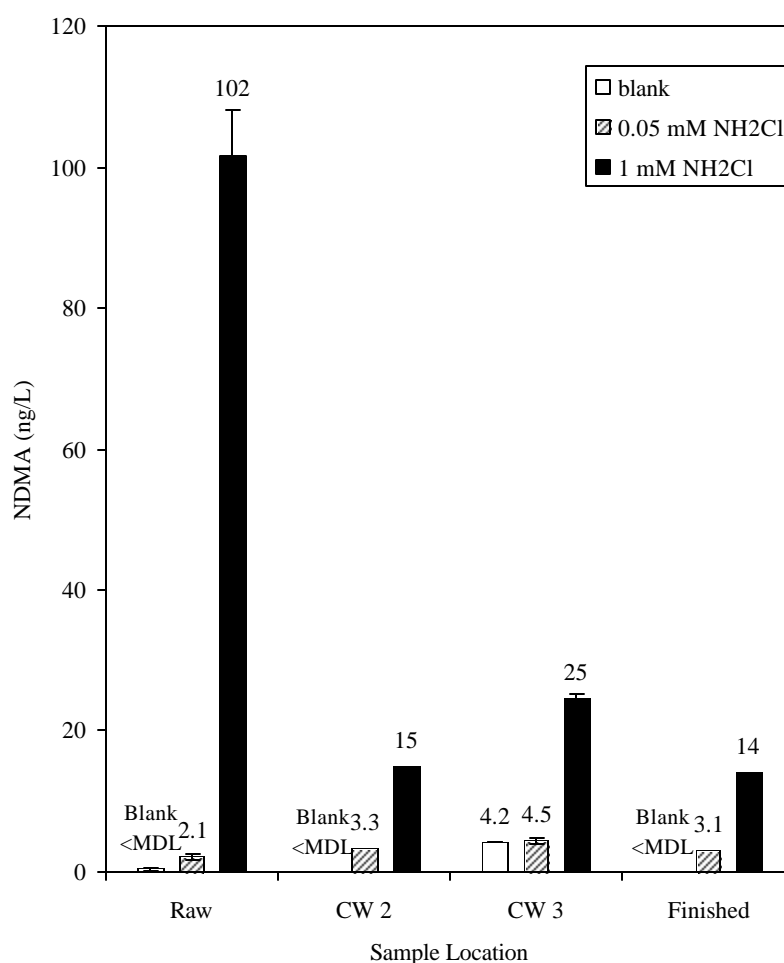


Figure 3. IC samples collected on 11-17-03. Monochloramine was added to the samples to produce a concentration in each reactor as indicated in the figure. Error bars are shown for reactors in which duplicates were run. All samples were incubated in the dark at  $20^\circ\text{C}$  for 7 days. The average pH of the bicarbonate buffered reactors was  $8.27 \pm 0.2$ .

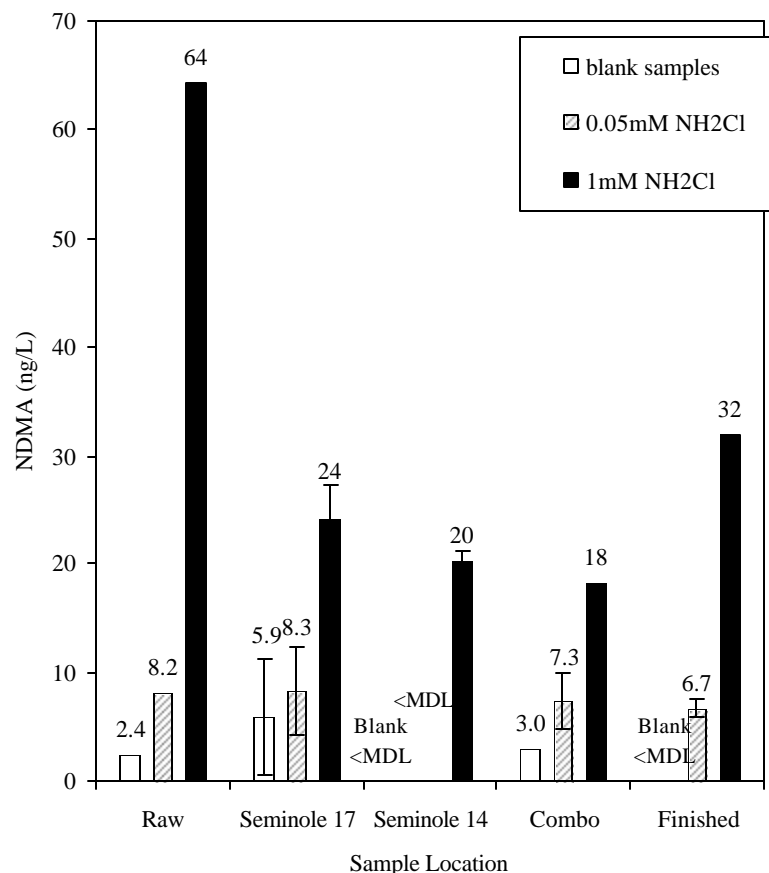


Figure 4. Cedar Rapids samples collected on 9-29-03. Monochloramine was added to the samples to produce a concentration in each reactor as indicated in the figure. Error bars are shown for reactors in which duplicates were run. All samples were incubated in the dark at 20°C for 7 days. The average pH of the bicarbonate buffered reactors was  $8.20 \pm 0.15$ .

**Mechanistic Studies: Role of DMA.** As little direct correlation was observed between NDMA FP and the agricultural indicator parameters, additional mechanistic studies were conducted to determine the role of DMA as a potential precursor of NDMA formation. DMA is a known NDMA precursor and a substance generally ubiquitous in water (Mitch and Sedlak, 2003). DMA was measured in samples obtained from four locations shown in Table 3, ranging from approximately 170 to 650 ng/L, supporting the notion that it could be an important precursor.

In order to determine the NDMA formed from observed levels of DMA, a controlled experiment was conducted to show how much NDMA could potentially be attributed to typical DMA levels measured in the water samples. DI water was spiked with 200 and 650 ng/L of DMA and preformed NH<sub>2</sub>Cl was dosed as in other parts of this study. The levels of NDMA formed were then compared with what was measured in the natural samples.

The NDMA measured in relation to DMA addition is shown in Table 3. These results indicate that DMA could account for only approximately 3-6% of the NDMA FP in the collected water samples. These relative yields are slightly higher, yet relatively consistent with the findings of Mitch and Sedlak (2004) who observed that the DMA present in their water samples could only account for approximately 0.6% of the NDMA FP (Mitch and Sedlak, 2003). Our results indicate that DMA does contribute to NDMA formation but that it cannot account for most of the NDMA formed. Therefore, other more important precursors must be present in these surface waters.

Table 3 Results of NDMA formation and DMA analysis for samples collected July, 2003 in relation not specific DMA addition to DI water. The % NDMA attributed to DMA concentrations in the water is based on the NDMA formed in the DI samples, assuming no other NDMA precursors were present in the DI water.

Site	NDMA ng/L	DMA ng/L	% NDMA from DMA
DI water pH~8	4.5	200.0	100%
DI water pH~8	7.0	650.0	100%
New Providence	129.6	196.3	3%
Rowan	77.5	170.6	6%
Wapello	90.4	174.0	5%
Tripoli	114.0	651.2	6%

**NDMA Precursor Exhaustion Study.** Determining the class of likely precursors (e.g., agricultural indicators or DMA) was previously discussed as part of this study; however, regardless of what the NDMA forming precursors are, it was relevant to conduct additional studies to determine the extent of precursor exhaustion based on the experimental methods used. The kinetics of  $\text{NH}_2\text{Cl}$  autodecomposition as delineated by Valentine and Jafvert at various pH values was used to calculate the concentration-time ( $\text{C}^*\text{t}$ ) curve for each assay.  $\text{C}^*\text{t}$  values were used to assess whether the observed disappearance of  $\text{NH}_2\text{Cl}$  over the course of each assay was due to reaction with precursor material in the samples or autodecomposition. Subsequent experiments measured  $\text{NH}_2\text{Cl}$  decay in DI water and Iowa River water under varying Cl/N ratios at the pH values relevant in this study. From these studies, monochloramine decay kinetics were measured and used to normalize NDMA formation potential to the calculated  $\text{C}^*\text{t}$  for each reactor.

An experiment to fully exhaust all NDMA precursors in the water samples was conducted to measure the NDMA formation after 7 and 14 days. Iowa River water was collected from the University of Iowa water treatment plant and filtered through the same  $1.6\ \mu\text{m}$  glass fiber filters used in other experiments. Batch reactors were comprised of roughly 500 ml of water, 1 mM  $\text{NH}_2\text{Cl}$  and either 10 mM phosphate or bicarbonate

buffers in order to maintain pH values around 7 and 8, respectively. Blank samples were not dosed with preformed  $\text{NH}_2\text{ClAs}$  in other experiments, measurements of  $\text{NH}_2\text{Cl}$  concentrations were measured on a daily basis for each reactor over the 7-day and 14-day reaction periods. Precursor exhaustion was therefore tested by comparing the amount of NDMA that could be formed by a second dosage of  $\text{NH}_2\text{Cl}$ , readjusting to the initial 1 mM  $\text{NH}_2\text{Cl}$  concentration, followed by 7 more days of incubation.

Based on the precursor exhaustion experiment performed, the majority of NDMA was formed within the first 7 days of the experiment. As shown in Figure 5, appreciable levels (between 5 and 21 ng/L) of NDMA are additionally formed after a subsequent respike of  $\text{NH}_2\text{Cl}$  which readjusted the concentration to 1 mM. Also, Table 4 shows the results of normalized NDMA formation ( $\text{NDMA}/\text{C}^*\text{t}$ ) based on the precursor exhaustion experiment. Due to the fact that the ratio of NDMA to  $\text{C}^*\text{t}$  is significantly reduced between the 7-day and 14-day reactors, it can be surmised that the NDMA formation precursors initially present in the surface water samples were mostly consumed within the first 7 days. If this were not the case, the second chloramine dosage would form similar amounts of NDMA as the first dosage and the  $\text{NDMA}/\text{C}^*\text{t}$  values would be closer.

This experiment was performed in order to provide a quantitative basis for past and future experiments involving the formation of NDMA in natural waters in conjunction with  $\text{NH}_2\text{Cl}$  decay. From the data measured, the Valentine Chloramine Stability coefficient for each reactor was measured and compared to theoretical calculations based on the average pH, initial and final  $\text{NH}_2\text{Cl}$  concentrations as well as the equilibrium coefficients associated with each buffer used. The normalization of NDMA formation with  $\text{C}^*\text{t}$  demonstrate how precursor limitation was experienced in all reactors dosed with 1 mM  $\text{NH}_2\text{Cl}$ . From this, the potential for various NDMA formation precursors can be suggested based on  $\text{NH}_2\text{Cl}$  demand.

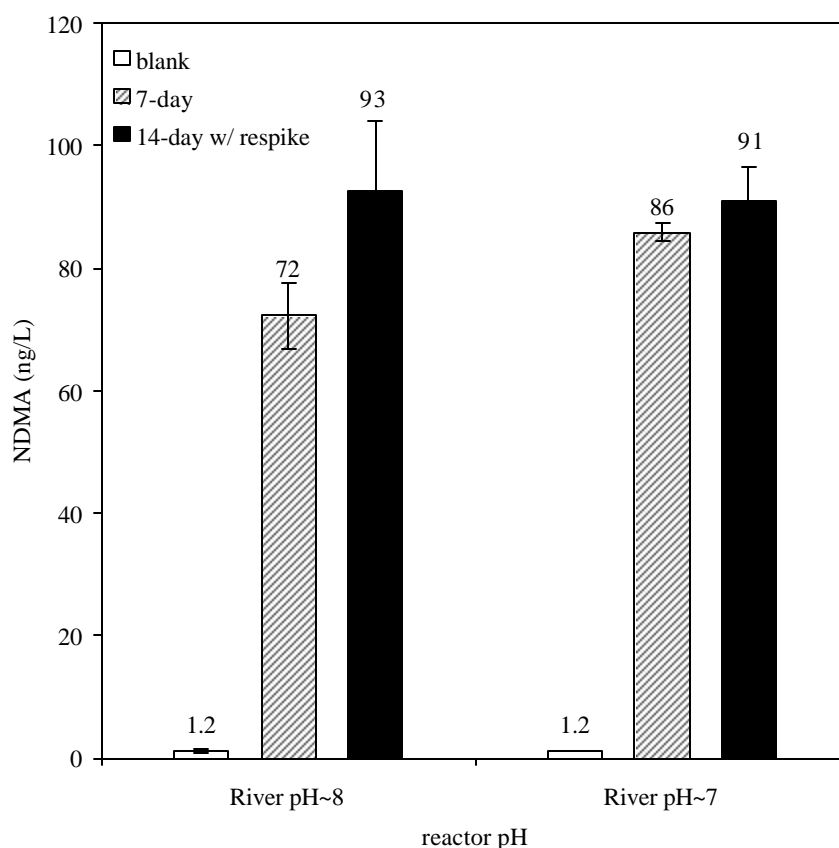


Figure 5. Precursor limitation experiment performed on 3-17-04 with filtered Iowa Riverwater. All samples were buffered with either 10 mM bicarbonate or phosphate buffers in order to maintain pH values around 8 and 7, respectively. All reactors were incubated in the dark at 20°C.

Table 4. Summary table of C\*t normalized NDMA formation (NDMA/C\*t) in Iowa River water at various pH values. The 7-day samples were dosed with 1 mM preformed NH<sub>2</sub>Cl and incubated in the dark at 20°C. The 14 day samples were amended with sufficient NH<sub>2</sub>Cl in order to readjust the concentration to the original 1 mM.

Sample	NDMA (ng/L)	C*t (mg Cl <sub>2</sub> -h/L)	NDMA/C*t	%NDMA formed in 7 days
7-day @ pH~8	72.3	8632	8.4	--
14-day @ pH~8	92.8	21874	4.2	78
7-day @ pH~7	85.8	6134	14.0	--
14-day @ pH~7	91.0	21431	4.2	94

## Summary and Conclusions

Results from this exploratory study demonstrate that a significant NDMA formation potential exists in the agriculturally impacted surface waters sampled. Measurements of NDMA formation potential in two typical Iowa drinking water sources and treatment facilities further suggest that chloramination practices may need to be assessed based on potential NDMA formation in the distribution system. Maximum NDMA formation values were based upon monochloramine dosages approximately 20 times that typically used in drinking water disinfection. NDMA was also formed at quantifiable levels when samples were dosed with monochloramine at concentrations typically used in drinking water treatment. The maximum NDMA FP for samples amended with the higher concentrations of monochloramine is typically in a range that can exceed 100 ng/L which is 10 times higher than that generally considered acceptable by any regulatory or health risk standards.

No statistical evidence was obtained that showed a significant difference in NDMA FP between the four agriculturally impacted watersheds over the course of this study when data was pooled over all the sampling periods. Seasonal trends for predicting variations in formation potential were distinguishable over the course of this preliminary study. Additionally, NDMA FP did not conclusively correlate with nitrate, organic nitrogen, or total organic carbon at any location. The determination of these statistical correlations was limited by the sample size available for each parameter over the course of the study as well as the relatively short time period available for data collection and analysis.

Dimethylamine was measured in selected agriculturally impacted watershed samples as an established NDMA forming precursor. Experiments conducted in this study corroborated other research which suggests that DMA is not the sole NDMA precursor present in surface waters. Results from this study revealed that the DMA content measured could account for only a relatively insignificant amount (approximately 3-6%) of the NDMA FP, suggesting that the presence of other precursors also existed in the samples.

The influence of riverbank filtration (RBF) on NDMA formation was studied at both low (0.05 mM) and high (0.5 or 1.0 mM) monochloramine dosage. NDMA formation was generally greater at the higher monochloramine dosages but this trend was not always the case. The high monochloramine 7-day NDMA formation potential in the raw water was approximately 100 ng/L in IC and between 40 and 60 ng/L in CR. Riverbank filtration generally reduced the NDMAFP in IC water by 90 % and between 30% and 80% in CR water, for the higher monochloramine dosage.

Significant amounts of NDMA were also formed by the addition of 0.05 mM monochloramine when measured against the 0.7 ng/L EPA  $10^{-6}$  cancer risk level. Raw water dosed with 0.05 mM  $\text{NH}_2\text{Cl}$  produced NDMA values of approximately 10 ng/L in IC water and 20 ng/L in CR water. Interestingly, neither RBF nor conventional surface water treatment techniques seemed to have a significant effect on reducing NDMA formation potential at the lower monochloramine dosage.

The study of NDMA formation from two sequential dosages of 1 mM  $\text{NH}_2\text{Cl}$  and two 7-day incubation periods support the hypothesis that most of the precursors present are exhausted after the first dosage and incubation period and the NDMA FP increased by only 5-10% after the second dosage. This may explain why NDMA FP did not correlate linearly with the concentration-time ( $C^*t$ ) values as it would if the precursor concentration were not reduced with monochloramine dosage. This may also explain why the NDMA FP was approximately the same at pH 7 and 8. While differences were observed in the NDMA FP between nominal pH values of 8 and 7, they were generally within approximately 10%. This may be attributable to near exhaustion of the NDMA precursors in both cases not necessarily reflective of identical formation kinetics.

From this research further work should be done to investigate precursors originally present in typical agriculturally impacted surface waters as well as additional compounds which may be introduced as a result of riverbank filtration and conventional drinking water treatment. Anthropogenic chemicals introduced in urban and agricultural watershed areas may both lead the augmentation of NDMA formation potential in source waters. The classification of NDMA formation potential should be recommended as part of future source water quality evaluations in newly designed treatment facilities located in potentially high risk areas. As a result of preliminary source assessments, alternative and or additional treatment strategies may be needed in order to reduce the risk of exposure to NDMA. Although this may increase the overall cost of treatment for a particular community, research presented here and in other studies demonstrates the importance of chronic NDMA exposure and the importance it plays in drinking water treatment.

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